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AUTHOR(S):

Petermann, Jürgen

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The Formation of Microstructures (morphologies) in Ultra-thin Films of Semi-crystalline Polymers*

Jürgen PETERMANN**

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Not only the crystallinity itself but also the shape of the crystals, their orientation and their self-assembly into larger units (e.g. spherulites) have considerable influence on the physical properties of semi-crystalline polymers. Since the dimensions (at least in one direction) of the crystals are in the nanometer range, the transmission electron microscopy (TEM) is an appropriate tool to investigate their arrangements and defects. Recently, the interest in ultra-thin films of polymers has increased due to their potential use in microelectronic devices, membranes and other new technologies, and morphologies in bulk samples may differ from those in thin films. Selected examples of morphologies in ultra-thin films are summarized.

KEY WORDS: Ultra-thin Films / Morphologies / Polymer crystals / Electron microscopy (TEM)

1. INTRODUCTION

The concept of controlling the microstructures of inorganic materials has led to the technological success of the advanced materials in metals, ceramics and semiconductors. Polymeric materials exhibit even wider possibilities for microstructural formations due to their large variety in molecular architectures, and many attempts have been made to correlate the molecular and supermolecular structures with bulk properties. Recently, the interest in ultra-thin layers has increased and new properties can be expected from those materials. Besides the surface free energy and the two-dimensionality which influence the morphologies in all thin film materials, the long chain nature of the macromolecules, where often the length of the macromolecules exceeds the thickness of the films, has additional influence on the morphologies in ultra-thin polymeric films.

Some selected examples of the morphologies in semi-crystalline polymers of ultra-thin films will be presented. The preparation of ultra-thin films is an art by itself and research groups are mostly specialized in one of the methods. Langmuir-Blodgett (LB) films and evaporation (physical vapour deposition) on substrate surfaces are among the most commonly used methods but will not be treated here.

2. SOLUTION CAST FILMS ON HOT LIQUID SURFACES

Depending on wettability of a surface, extremely thin polymer films (<40 nm) can

* Dedicated to Prof. Dr. Ken-ichi Katayama

** Jürgen Petermann: TU Hamburg-Harburg, Polymer Composites Group, Harburger Schloßstraße 20, D-2100 Hamburg 90, Germany

be casted from dilute solutions.¹⁾ The resulting morphologies are strongly influenced by the temperature of the surface. For getting reproduceable results, the temperature of the surface should be above the melting point of the polymer in order to avoid precipitation of polymer crystals during the evaporation of the solvent. Also, the structure and topology of the surface influences the crystallization of the polymer (see below) when cooling it below the crystallization temperature. Liquids (as orthophosphoric acid, glycerol or molten ionic salts) can fulfill the requirements of structure, topology and temperature of those surfaces.

When the thickness of the molten films does not exceed the thickness of solution grown single crystals by more than a factor of about three, and the supercooling $\Delta T = (T_m - T_c)$ is low, macromolecular orientations with the direction of the macromolecules perpendicular to the surface develop (single crystal-like orientation). In Fig. 1a, the electron diffraction pattern of isotactic polystyrene (iPS) crystals are shown and Fig. 1b is a dark field TEM picture of this crystal. On some parts of the



Fig. 1a Electron diffraction from an iPS single crystal (grown at 220°C).

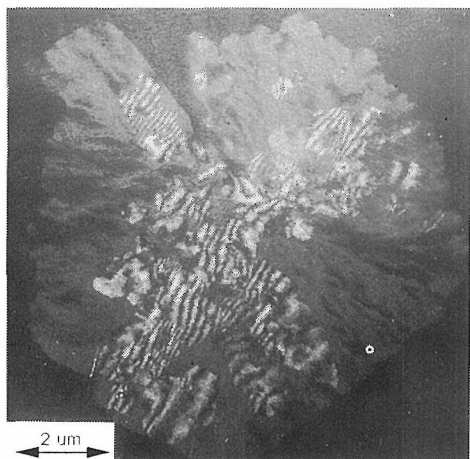


Fig. 1b TEM dark field photograph from an iPS single crystal (grey areas). The dark/bright fringes are moiré patterns, resulting from overgrown crystals.

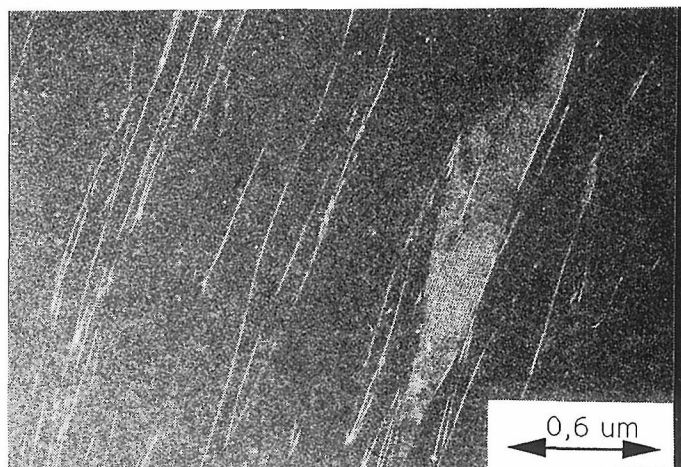


Fig. 2 TEM dark field photograph from iPS. The bright lines are edge-on lamellae, the bright area consists of two overlapped single crystals (moiré patterns). The sample was crystallized at 190°C.

crystal moiré patterns are seen, resulting from a second superimposed crystal. At higher supercooling, crystal lamellae oriented edge-on begin to form, with single-crystal-like orientation in the areas between the edge-on lamellae (Fig. 2). At even higher supercooling and/or in thicker films, two dimensional spherulites develop (Fig. 3a).²⁾ The morphologies themselves do not change with heat treatments at elevated temperatures, but local crystal melting (Thomson melting) can be observed. This is demonstrated in Fig. 3b, where a two dimensional spherulite (compare Fig. 3a) was annealed close to the melting range, and the edge-on lamellae of the spherulite are disrupted in their crystalline continuity.

3. HIGHLY ORIENTED THIN FILMS

Since physical properties of polymers on the nanometer scale are very anisotropic (mechanical strength, thermal conductivity and expansion, a.o.), orientational order of the macromolecules above the nanometer scale are often required for practical

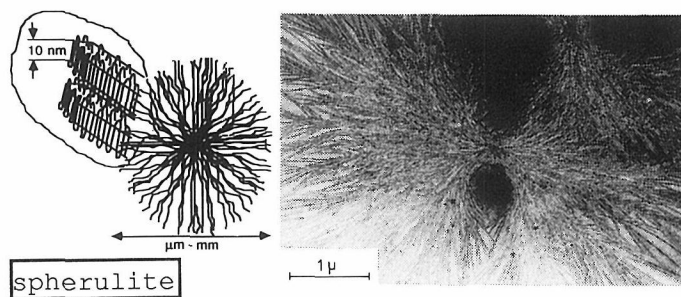


Fig. 3a TEM bright field photograph (defocus contrast) of a two dimensional spherulite in iPS, grown at 150°C.

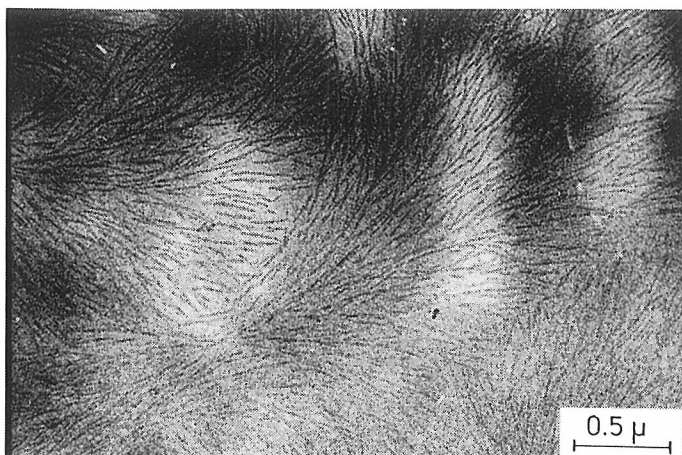


Fig. 3b TEM bright field photograph of iPS spherulites, grown at 150°C and subsequently annealed at 190°C.

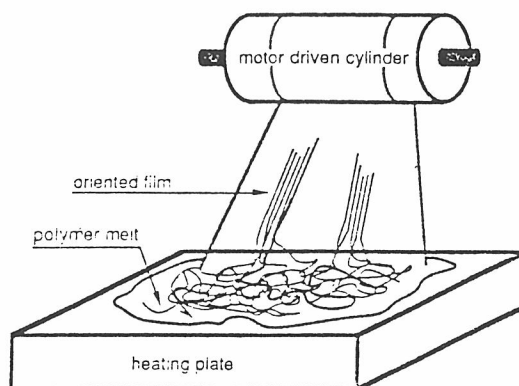


Fig. 4 Schematic sketch of the preparation technique of oriented ultra-thin films.

purposes. Uniaxial orientation of the macromolecules in ultra-thin films can be obtained by a simple "film stretching" method³⁾ (Fig. 4). Depending on straining condition, different morphologies can be obtained with all of them having in common that the direction of the macromolecules is in straining direction. High temperature of the non-strained molten film with using small strain rates results in a stacked lamellar morphology (Fig. 5a), high temperature with high strain rates in a needle-like morphology (Fig. 5b) and low temperature with high strain rates in an oriented micellar morphology (Fig. 5c). The transition between these morphologies is more or less continuous and a mixture of the morphologies can also be obtained (Fig. 5d). Details of these morphologies on the molecular range were investigated using high resolution TEM. Pioneering work in this field has been performed by K. Katayama et. al. of the "Polymer Crystal laboratory" at the Institute of Chemical Research, Kyoto University.⁴⁻⁶⁾

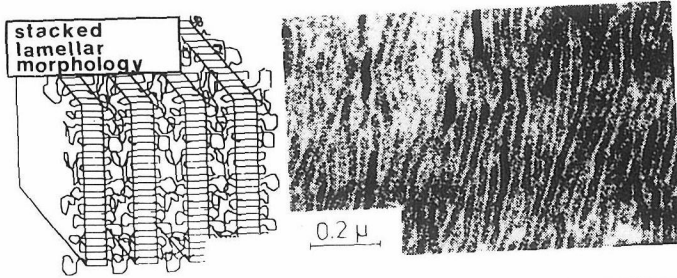


Fig. 5a Stacked lamellar morphology in PE (TEM bright field).

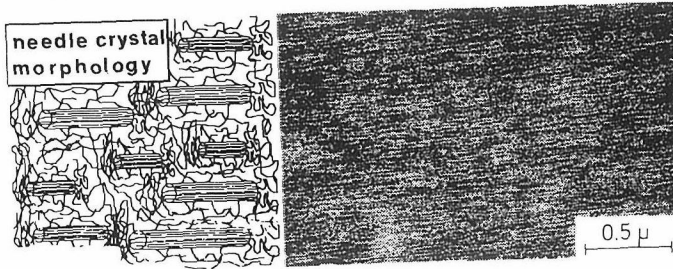


Fig. 5b Needle-like morphology in polybutene-1 (TEM bright field).

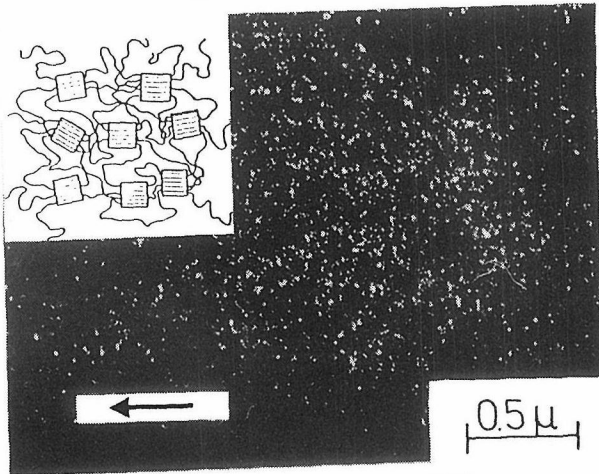


Fig. 5c Oriented micellar morphology in polyethyleneterephthalate (PET), TEM dark field micrograph.

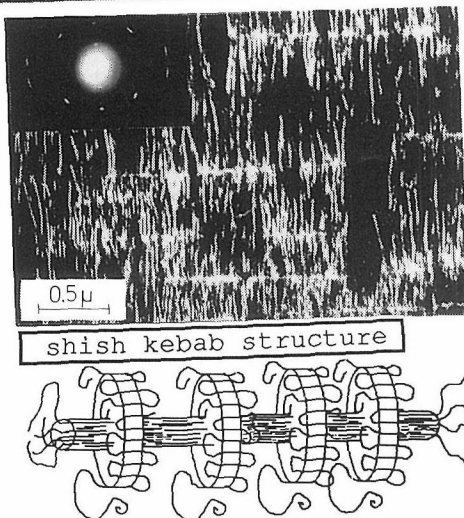


Fig. 5d Shish-kebab morphology in iPS (TEM dark field micrograph).

4. TRANSITION LAYERS IN POLYMER INTERFACES

As mentioned earlier, the morphology of thin films crystallized on a substrate surface is influenced by the topology and structure of the surface. The direction of heat flow during the crystallization event may also lead to specific morphologies in the surrounding of the interface. Well known is the epitaxial crystallization, characterized as an oriented overgrowth of a crystalline phase upon the surface of another crystalline substrate, caused by a positional matching of atoms or molecules of both substances in specific crystallographic lattice planes.⁷⁾ Epitaxy of solution crystallized polymers on the surfaces of ionic salts or molecular crystals has been known since long time⁸⁾ and has also been observed during polymerization events.⁹⁾ Generally, epitaxy of polymer crystals on non-polymer substrates is very well established. On the contrary, epitaxy of polymeric and non-polymeric crystals on the surfaces of polymer substrates has found interest just recently.¹⁰⁻¹⁴⁾ Experimental difficulties in preparing crystallographic well specified surfaces of the polymer substrates have been among the obstacles in those investigations. Recently, ultra-thin films of uniaxially oriented isotactic polypropylene (iPP) has been used as a surface and epitaxial-like crystallization of polyethylene (PE) was observed^{10,11)} on the surface of these substrates (Fig. 6a,b). The concept of positional matching of the iPP and PE molecules in the interface cannot be accounted as straightforward as it is used successfully in the interpretation of epitaxial crystallization of non-polymeric crystals for several reasons:¹⁵⁾ among which are that the substrate (iPP) surface is not belonging to a single crystal but consists out of microscopically small (hko) lattice planes only having the $[001]$ lattice direction in common, and the monoclinic (α -phase) crystal modification or the trigonal crystal modification (β -phase) of the iPP substrate films do not alter the crystallographic orientation relationship to the overgrown PE films.

Similar epitaxial-like crystallization of other polymeric materials onto polymeric substrates has been reported recently.¹⁵⁾ Also, epitaxial crystallization of short chain molecules onto the surfaces of several uniaxially oriented polymer substrates were investigated,¹⁴⁾ using either the method of crystallizing ultra-thin molten films or physical vapor deposition of the short chain molecules. These methods of epitaxial-like crystallization of ultra-thin films can be considered as an alternative to the Langmuir-Blodgett film techniques. Additionally, the investigations of the formation of those oriented (epitaxial) polymer films may help in the understanding of nucleation and interface adhesion in polymeric materials. Further detailed information for molecular interactions at interfaces may be obtained with the scanning tunneling microscopy techniques (STM).¹⁶⁾ Fig. 7 shows a STM micrograph from an oriented ultra-thin PE film.¹⁷⁾ The straight lines may represent single stretched PE chains.¹⁸⁾ The contrast formation from electric insulating polymer chains on pyrolytic graphite in the STM techniques is still not understood and further experiments have to be carried out in order to interpret the micrograph (Fig. 7) correctly.

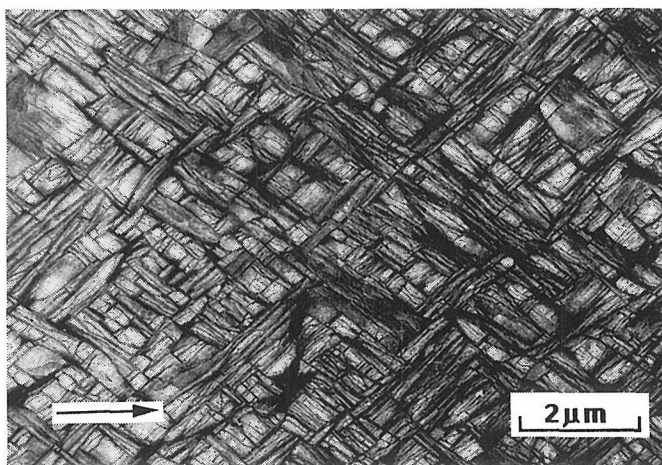


Fig. 6a Oriented crystallized PE (cross-hatched pattern) onto uniaxially oriented iPP. Crystallization temperature for the PE is 113°C.

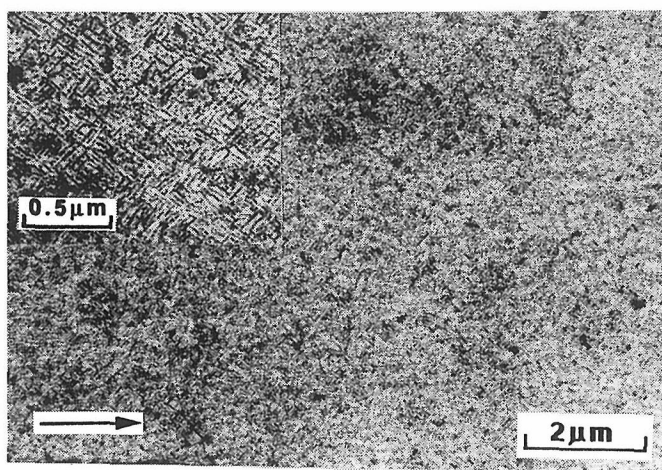


Fig. 6b As Fig. 6, but crystallization temperature 0°C.

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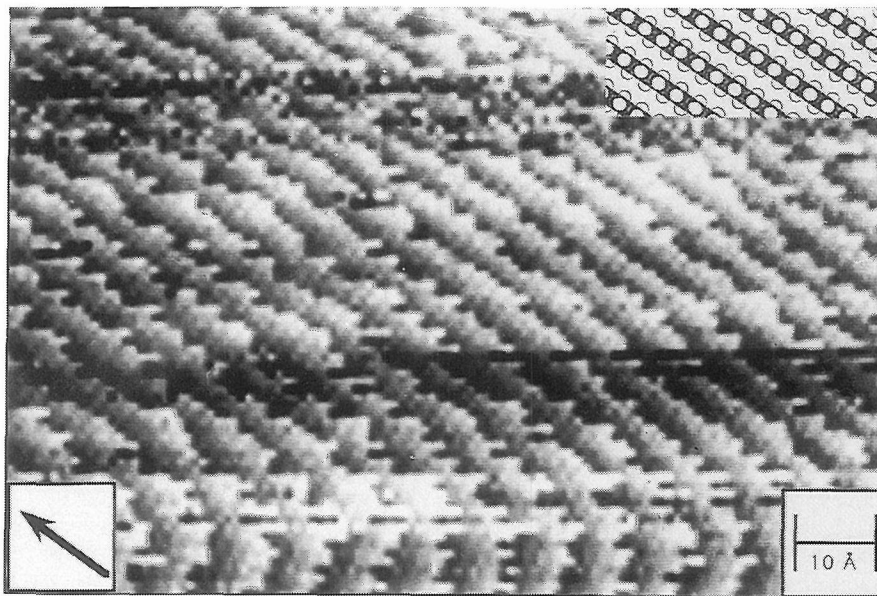


Fig. 7 STM micrograph of oriented PE.

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